

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 April 2004 (15.04.2004)

PCT

(10) International Publication Number
WO 2004/031448 A1

- (51) International Patent Classification⁷: C23F 1/44, F01D 5/00, 25/00
- (21) International Application Number: PCT/EP2003/010988
- (22) International Filing Date: 1 October 2003 (01.10.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: MI2002A002090 3 October 2002 (03.10.2002) IT
- (71) Applicant (*for all designated States except US*): NUOVO PIGNONE HOLDING S.P.A. [IT/IT]; Via F. Matteucci, 2, I-50127 Florence (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): ANSELM, Marco [IT/IT]; Via Faentina, 57, I-50133 Florence (IT). BANNINI, Alessio [IT/IT]; Via del Risorgimento, 124, I-50019 Sesto Fiorentino (IT). STEFANELLI, Marco [IT/IT]; Piazza Giuseppe di Vittorio, 13, I-59016 Poggio A Caiano (IT). KOOL, Lawrence [US/US]; 2 Cardinal Court, Clifton Park, New York, NY 12065 (US).
- (74) Agents: COPPO, Alessandro et al.; Ing. Barzano' & Zarnardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: AQUEOUS COMPOSITION FOR THE CHEMICAL REMOVAL OF METALLIC SURFACING PRESENT ON TURBINE BLADES, AND ITS USE

(57) Abstract: An aqueous composition for the chemical removal of metallic surfacing present on the blades of turbines, preferably gas turbines, comprises at least hexafluorosilicic acid and phosphoric acid.

WO 2004/031448 A1

5

AQUEOUS COMPOSITION FOR THE CHEMICAL REMOVAL OF METALLIC
SURFACING PRESENT ON TURBINE BLADES, AND ITS USE

The present invention relates to an aqueous composi-
10 tion for the chemical removal of metallic surfacing pres-
ent on turbine blades, and its use.

In particular, the invention relates to an aqueous
composition for the chemical removal of metallic surfac-
ing present on gas turbine blades.

15 Gas turbine refers to the rotary heat engine unit
which converts the enthalpy of a gas into useful work,
using gas coming directly from combustion and which sup-
plies mechanical power to a rotating shaft.

A turbine therefore usually comprises one or more
20 compressors or turbo-compressors, into which air from the
outside is brought under pressure.

Various injectors feed the fuel which is mixed with
air forming an air-fuel primer mixture.

The axial compressor is piloted by an actual tur-
25 bine, or turbo-expander, which supplies mechanical energy

to a user transforming the enthalpy of gases combusted in the combustion chamber.

A turbo-expander, turbo-compressor, combustion chamber (or heater), mechanical energy outlet shaft, regulation system and activation system form the essential parts of a gas turbine plant.

As far as the functioning of a gas turbine is concerned, it is known that the fluid penetrates the compressor through a series of inlet ducts.

10 In these channels, the gas has low pressure and temperature properties, whereas as it passes through the compressor, it is compressed and its temperature increases.

It then penetrates into the combustion (or heating) chamber, where it undergoes a further significant increase in temperature.

The heat necessary for increasing the temperature of the gas is supplied by the combustion of the liquid fuel introduced into the heating chamber, by means of injectors.

20 At the outlet of the combustion chamber, the gas, at a high temperature and pressure, reaches the turbine, through specific ducts, where it releases part of the energy accumulated in the compressor and heating chamber (combustor) to the turbine blading and consequently to

the shaft and then flows out through discharge channels.

As the work transferred by the gas to the turbine is greater than that absorbed thereby in the compressor, a certain quantity of energy remains available, on the machine shaft, which, deprived of the work absorbed by the accessories and passive resistances of moving mechanical organs, forms the useful work of the plant.

Turbines destined for high power production are generally multi-step in order to optimize the yield of the transformation of energy rendered by the gas into useful work.

Each step of the turbo-compressor and turbo-expander is designed to operate under certain conditions of pressure, temperature and gas rate.

It is also known from thermodynamics that, in order to obtain the maximum yield from a certain gas turbine, the temperature of the gas must be as high as possible.

As a result of the pressure and temperature conditions and rate of the rotating organs, it is evident that the blading undergoes particular stress and is therefore subject to rapid deterioration due to wear.

Among the various types of wear to which the blades are subjected, wear by erosion can be mentioned, in particular at a high temperature, mainly caused in gas turbines by the impact of solid particles contained in the

combustion fumes on the surface of the blade.

This phenomenon is complicated by the fact that the mechanical resistance of a material does not guarantee its resistance to wear and its characteristics must be specifically studied to enable the effects to be minimized; furthermore the properties of the erosive particles are also important and are a fundamental parameter in controlling this type of wear.

As a result of the aggressiveness of the gases, a chemical attack of the surface layer of the blades can be easily predictable, causing so-called corrosive wear, in particular under heat.

Under the operating conditions of gas turbines, the existence of oxidative wear caused by the presence of oxygen not consumed during combustion, is also inevitable.

The wear mechanism in operating situations such as those of turbine blades is, however, extremely complex and other forms or wear mechanisms can also be involved. Typical examples are wear-melting which takes place when the contact forces and rates are sufficiently high as to melt the first surface layers of the solid, and wear-diffusion obtained when the temperatures at the interface are high.

In order to avoid the rapid deterioration of me-

chanical blades subjected to the above severe forms of wear and consequently prolong the useful life, high-resistant materials such as super-alloys, for example based on nickel-chromium and nickel-cobalt, were first
5 proposed.

It was verified however that the increase in operating temperatures necessary for raising the power and performance of the machine, caused excessive oxidation in the super-alloys used for the blades of the turbine and
10 compressor.

This drawback created the necessity for providing protective coatings specifically studied for these super-alloys and for resisting the operating conditions.

Without entering into detail with respect to the
15 various coating processes of super-alloys, we would only like to mention that they can be divided into two main categories: those which imply alteration of the outermost layer of the substrate with its contact and interaction with the chemical species selected (diffusion coating
20 processes), and those which imply deposition of the protective metallic species on the surface of the substrate with adhesion provided by a lower amount of inter-diffusion of elements (overlay coating processes).

These surfacings of the metallic type, which coat
25 the metallic alar surface of gas turbine blades exter-

nally and internally, generally consist of Platinum-Aluminum-Nickel-Cobalt-Chromium-Yttrium or Cobalt-Chromium-Aluminum-Yttrium or Nickel-Cobalt-Chromium-Aluminum-Yttrium.

5 On the whole, as regards the evolution of Me-CrAlY coatings, wherein Me refers to one of the metals cited above, such as Pt, Co etc., applied to Ni-based super-alloys, one of the main damaging mechanisms is due to an impoverishment of the Al contained in the Ni, Co, Al
10 phase distributed in the matrix of the coating.

 In order to feed the reformation process of the protective scale of Al_2O_3 oxide which is removed by erosion or acid dissolution during functioning, said phase (Ni, Co, Al) present in the coating breaks up releasing the
15 necessary Al.

 Diffusion processes of the Al released consequently take place both towards the outside surface and also with respect to the base metal.

 The result is that, as the functioning proceeds, the
20 layer of coating containing the above phase (Ni, Co, Al) progressively thins out, remaining confined in a central area of the coating itself.

 In addition to the impoverishing effects of this phase (Ni, Co, Al), corrosion-erosion phenomena can lead
25 to a significant reduction in the thickness of the coat-

ing.

The two impoverishment parameters of the phase and residual thickness should therefore be considered as the main indicators of the residual life of MeCrAlY coatings.

5 It can consequently be understood how the aggressiveness of the corrosion and oxidation phenomena on the hot parts of gas turbines becomes more significant with a rise in the operating temperature in order to obtain an increase in the power and performance of the machine.

10 For this reason, high temperature coatings which guarantee the protection of blades of the first steps with respect to these phenomena, are becoming increasingly essential components.

During the functioning of the blades, as a result of
15 the severe operating conditions, also these surfacings are subject to the formation of cracks and damage in general and must therefore be frequently checked and controlled.

This control of the blades must be extended to the
20 underlying surfaces of the surfacing layers consisting of the super-alloy base, and it is therefore necessary to remove the surfacing layers for varying thicknesses in order to check the base material and subsequently re-establish the original thickness by means of a new layer
25 of surfacing on the base material.

The removal, also called "stripping", of the metallic surfacings is, in any case, required for all testing and restoration activities of the blades operating in gas turbines.

5 This process can be effected both chemically and also, at least theoretically, mechanically.

Mechanical removal, however, is definitely not a particularly reliable technology as even if the mechanical removal action is effected with accurate methods and
10 means, it also damages the base material, jeopardizing the resistance of the blades themselves and, in addition, it cannot be adopted for surfacings applied inside the cooling cavities and holes of the blades.

Chemical removal is suitable for the removal surfacings both inside and outside the blades.
15

The main drawback of the chemical substances used according to the known art for these applications is that they are excessively aggressive also for the base materials forming the blades themselves.

20 As the thickness of the surfacings is of a reduced entity, from a few microns to a maximum of about 2 tenths of a millimeter, there are frequently cases in which the base alloy forming the blades is chemically attacked, during the chemical removal process, by the acid solutions used, with consequent irreparable damage to the
25

blades themselves.

The main objective of the present invention is therefore to overcome the above drawbacks of the known art by providing an aqueous composition capable of chemically removing the metallic surfacing present on the alar
5 surfaces of the blades of turbines in particular gas turbines, without causing damage to the underlying material.

The objectives of the present invention also include the use of the above aqueous composition for obtaining
10 the removal of metallic surfacing present on the blades of gas turbines.

These and other objectives, according to the invention, are achieved by an aqueous composition for the chemical removal of metallic surfacing present on the
15 blades of turbines, in particular gas turbines, and its use for the chemical removal of metallic surfacing present on the blades of turbines, in particular gas turbines.

The invention proposes the use of a selective aqueous composition comprising at least hexafluorosilicic
20 acid and phosphoric acid for the removal of surfacing of blades, both internal and external, without damaging the base alloys forming the blades themselves even when exposed to moderately prolonged contact with time with the
25 chemical solution.

The composition according to the invention is obtained by mixing at least hexafluorosilicic acid or fluo-
silicic acid (chemical formula H_2SiF_6) with phosphoric
acid (chemical formula H_3PO_4) in dosage percentages which
5 are such as to obtain a final composition corresponding
to that which can be obtained by mixing an aqueous solu-
tion of hexafluorosilicic acid at about 34% in a quantity
varying from 46% to 86% by volume with an aqueous solu-
tion of phosphoric acid at about 75% in a quantity vary-
10 ing from 19% to 49% by volume.

When the blade has a surfacing comprising Nickel
and/or a particularly oxidized surfacing, in order to ob-
tain an effective and selective chemical removal, the
aqueous composition according to the invention also com-
15 prises fuming hydrochloric acid at about 37% in aqueous
solution added in a quantity varying from 0% to 15% by
volume.

The percentage of hydrochloric acid solution should
therefore be considered as being additional to the total
20 volume of the bath.

The terms "at about 34%" referring to hexafluoro-
silicic acid, "at about 75%" referring to phosphoric acid
and "at about 37%" referring to hydrochloric acid, indi-
cate a certain variability in the composition of starting
25 reagents which can be estimated at about 3-5% by weight

of the aqueous solution of reagents, consequently the effective weight percentage of hexafluorosilicic acid, for example, from the declared titer of 34%, can be between 34% and 35% and even more in relation to the commercial
5 availability.

The same thing can be said for the other reagents and other starting titers; it should be pointed out that as far as hydrochloric acid is concerned, 37% represents the upper concentration limit which can be practically
10 obtained.

These reagents can be produced, moreover, with different processes and still have different titers and consequently, although the invention has been embodied with reagents in the concentrations indicated above, it is
15 possible, remaining included in its scope, to use, in the composition according to the invention, higher percentages of more diluted reagents and vice versa lower percentages of more concentrated reagents to obtain an aqueous composition having the above-mentioned concentrations
20 of reagents.

In other words, the titer of the starting reagents can vary in relation to the productive process of said reagents and can also have very different concentrations, such as for example hexafluorosilicic acid, which can be
25 found in aqueous solution with titers varying from 22% to

25% and again from 34% to 35% and yet again from 37% to 42%, to quote just a few possibilities.

The composition according to the invention is therefore also appropriately expressed in relation to the operating quantities in which it is used, bearing in mind that the so-called "bath" in which the blades to be treated are immersed, as an illustrative but non-limiting example, can have a volume in the order of 1000 litres.

From what has been specified, an aqueous composition according to the invention comprises at least hexafluoro-
silicic acid and phosphoric acid in the following concentrations: hexafluorosilicic acid from 156.4 g/l to 292.4 g/l; phosphoric acid from 142.5 g/l to 367.5 g/l.

If necessary, as previously mentioned, a further addition of hydrochloric acid is effected in a concentration substantially varying from 0 to 48.3 g/l in the specific case mentioned of a 1000 litre bath by respectively adding from 0 to 150 litres of fuming hydrochloric acid solution at 37%, to the composition initially obtained, thus obtaining a final bath with a volume substantially ranging from 1000 to 1150 litres with the above concentrations expressed on the basis of the overall volume of the bath.

The composition obtained is used for the removal of metallic surfacing on gas turbine blades heated to tem-

peratures ranging from 60°C to 90°C for operating times varying from 4 to 15 hours.

The preparation process of the aqueous composition according to the invention envisages at least a first
5 mixing phase of hexafluorosilicic or fluosilicic acid (chemical formula H_2SiF_6) with phosphoric acid (chemical formula H_3PO_4).

This preparation process of the composition according to the invention can be integrated with a further
10 mixing phase of fuming hydrochloric acid at 37% in aqueous solution in a quantity varying from 0% to 15%.

The present composition is preferably used for the removal of metallic surfacing layers on gas turbine blades, said use is described in the following example
15 with reference to the enclosed figure illustrating the results of a removal test of the surfacing layer of a gas turbine blade.

In particular, the enclosed figure shows the thickness removed of a Nickel-Cobalt-Chromium-Aluminum-Yttrium
20 surfacing on a gas turbine blade in relation to the time, using the aqueous composition according to the invention.

EXAMPLE

A Nickel-Cobalt-Chromium-Aluminum-Yttrium surfacing on a gas turbine blade was treated with an aqueous composition obtained by mixing hexafluorosilicic acid in aque-
25

ous solution at 34% with phosphoric acid in aqueous solution at 75% in dosage percentages as mentioned above.

The final aqueous composition thus obtained, heated to a temperature of 60°C was kept in contact with the surfacing layer by immersion of the gas turbine blade for a time of 15 hours thus obtaining the removal of the surfacing layer, expressed in relation to the immersion time and illustrated by the curve trend indicated in the figure.

10 Said removal varies from a value of 42 microns (μm) after 4 hours of immersion of the blade in the composition to a value of 153 microns (μm) after 15 hours of treatment.

15 From a micrographic test carried out after the treatment, no visible damage of the base alloy layer forming the blade was observed.

CLAIMS

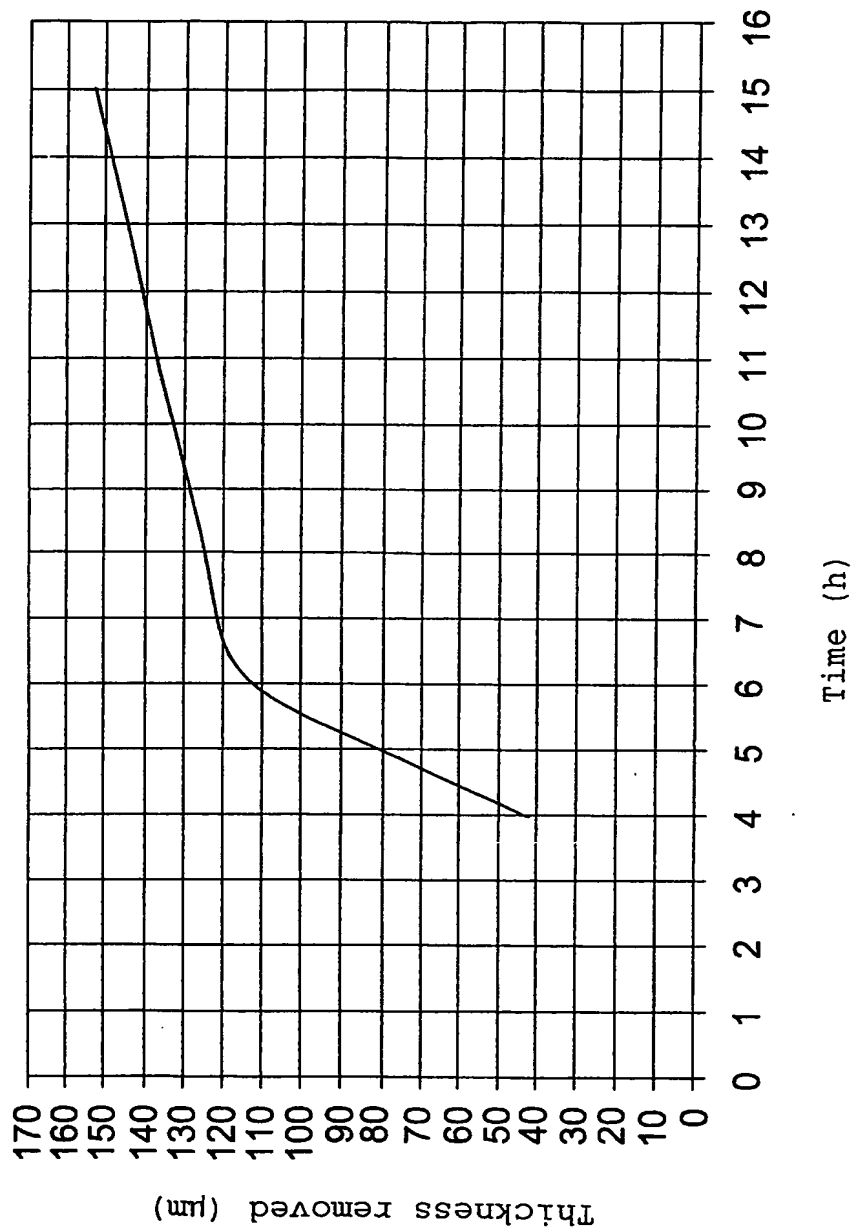
1. An aqueous composition for the chemical removal of metallic surfacing present on blades of turbines comprising at least hexafluorosilicic acid and phosphoric acid
5 whose final composition corresponds to that which can be obtained by mixing an aqueous solution of hexafluorosilicic acid at about 34% in a quantity varying from 46% to 86% by volume with an aqueous solution of phosphoric acid at about 75% in a quantity varying from 19% to 49%
10 by volume.

2. The aqueous composition according to claim 1, wherein said aqueous composition also comprises hydrochloric acid in aqueous solution at about 37% added in a quantity substantially varying from 0% to 15% of the volume of the bath obtained.
15

3. An aqueous composition for the chemical removal of metallic surfacing present on the blades of turbines comprising at least hexafluorosilicic acid and phosphoric acid in the following concentrations: hexafluorosilicic acid from 156.4 g/l to 292.4 and phosphoric acid from
20 142.5 g/l to 367.5 g/l.

4. The aqueous composition according to claim 3, wherein said aqueous composition also comprises hydrochloric acid in a concentration substantially varying
25 from 0 to 48.3 g/l.

5. Use of the aqueous composition according to any of the previous claims for the removal of metallic surfacing on gas turbine blades.
6. Use of the aqueous composition according to claim 2 or 4 for the removal of metallic surfacing comprising nickel and/or oxidized metallic surfacing on gas turbine blades.
7. Use of the aqueous composition according to claim 5 or 6, wherein said composition is used at a temperature ranging from 60°C to 90°C.
8. Use of the aqueous composition according to claim 5 or 6, wherein said composition is used for a time ranging from 4 hours to 15 hours.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/10988

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23F1/44 F01D5/00 F01D25/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23F F01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 162 286 A (GEN ELECTRIC) 12 December 2001 (2001-12-12) claims 1-8; examples 2,4 ---	1-8
X	FR 950 328 A (WETTINGHOUSE ELECTRIC) 23 September 1949 (1949-09-23) examples I,II ---	1-4
A	EP 1 050 604 A (GEN ELECTRIC) 8 November 2000 (2000-11-08) claims 1-6 ---	5,6
A	US 3 622 391 A (BALDI ALFONSO L) 23 November 1971 (1971-11-23) claim 1 ---	5,6
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

30 January 2004

Date of mailing of the international search report

06/02/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Torfs, F

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 85/10988

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 514 407 A (MISSEL LEO) 26 May 1970 (1970-05-26) claims 1,2; example 1 -----	1,3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP03/10988

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1162286	A	12-12-2001	EP 1162286 A1	12-12-2001
			JP 2002053985 A	19-02-2002
FR 950328	A	23-09-1949	US 2501349 A	21-03-1950
			GB 628054 A	22-08-1949
EP 1050604	A	08-11-2000	US 6494960 B1	17-12-2002
			BR 0007123 A	03-07-2001
			CA 2307398 A1	03-11-2000
			EP 1050604 A1	08-11-2000
			JP 2001003184 A	09-01-2001
			SG 91274 A1	17-09-2002
US 3622391	A	23-11-1971	NONE	
US 3514407	A	26-05-1970	NONE	